

Fate and transport of 1278-TCDD, 1378-TCDD, and 1478-TCDD in soil–water systems

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Abstract

The most toxic dioxin is 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2378-TCDD), and obtaining comprehensive experimental data for this compound is challenging. However, several nontoxic isomers of 2378-TCDD exist, and can provide significant experimental evidence about this highly toxic dioxin. The goal of this study was to obtain experimental evidence for the fate and transport of 2378-TCDD in natural soils using its nontoxic isomers, 1,2,7,8-tetrachlorodibenzo-*p*-dioxin (1278-TCDD), 1,3,7,8-tetrachlorodibenzo-*p*-dioxin (1378-TCDD), and 1,4,7,8-tetrachlorodibenzo-*p*-dioxin (1478-TCDD). Batch sorption and miscible-displacement experiments, in various soils, were done using [4-¹⁴C]-radiolabeled TCDDs, while metabolism of these compounds was monitored. The results from the batch experiments indicated a high sorption affinity of all the TCDD isomers to soils and a strong correlation to organic matter (OM) content. 1278-TCDD, 1378-TCDD and 1478-TCDD (TCDDs) were more tightly bound to the soil with high OM than to the soil with low OM; however, it took a longer contact time to approach sorption equilibrium of TCDDs in the soil with high OM. Miscible-displacement breakthrough curves indicated chemical nonequilibrium transport, where there was a rate-limited or kinetic sorption that was likely caused by OM. Combustion analyses of extracted soil from the soil columns showed that most TCDDs were adsorbed in the top 1–5 cm of the column. These column combustion results also showed that sorption was correlated to specific surface and soil depth, which suggested the possibility of colloidal transport.

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1. Introduction

Dioxins are chemical contaminants that are released into the environment by low temperature combustion processes, such as waste incineration, metal processing, and natural forest fires. The dioxin 2378-TCDD (Fig. 1) is the most toxic dioxin and causes a series of health

effects, which include reproductive and immunotoxicological effects at low-level exposure (Mably et al., 1991; Vos et al., 1991). Environmental exposure concentrations of 1 ng g^{−1} 2378-TCDD in soil were considered “a level of concern” for causing cancer (Pohl et al., 1995). Exposure concentrations in Times Beach, MO were reported as high as 1600 ng g^{−1} 2378-TCDD (Walters and Guiseppi-Elie, 1988). When 2378-TCDD is released into the soil it undergoes several fate and transport processes, which have been reported by various researchers. Walters and Guiseppi-Elie (1988)

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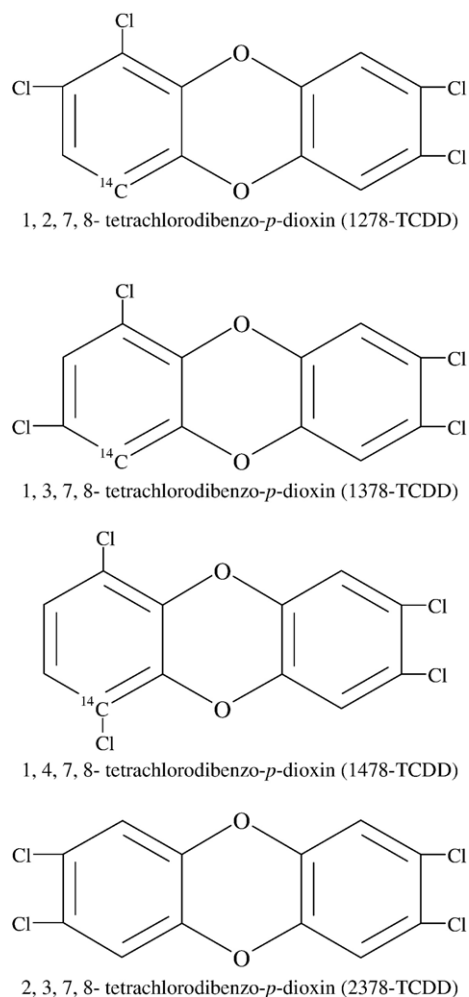


Fig. 1. Structures of 1278-TCDD, 1378-TCDD, 1478-TCDD, and 2378-TCDD. The radiolabeled carbons were located in the position 4.

and Walters et al. (1989a,b) did fate and transport experiments on 2378-TCDD and other polychlorinated dibenzo-*p*-dioxins using batch and saturated-flow soil column experiments with low-carbon soil materials. They found that a 5- to 10-day contact period was needed to achieve sorption equilibrium for 2378-TCDD in the soil with low organic materials. Their 2378-TCDD sorption-isotherms were all found to be linear, and sorption was correlated to the fraction of methanol in the liquid phase and to the soil type. Longer contact times were required for their soils with the higher OM than for their soils with low OM. Overcash et al. (1991) modeled 2378-TCDD movement through a soil column in which an organic co-solvent was present. Their model considered diffusive transport in the liquid phase and took into account the rate of sorption and desorption of 2378-TCDD from the soil particles. Their model

indicated that the movement of 2378-TCDD through soil with organic solvents could only be predicted when sorption and desorption rate constants, measured or estimated diffusion coefficient, and tortuosities were considered.

Although some studies have researched the adsorption of 2378-TCDD in soil, the fate and transport of this dioxin in the environment is still not fully understood. One reason for this is the lack of complete experimental data of this toxic compound in soil. Comprehensive data is difficult and expensive to obtain because of 2378-TCDD's high toxicity. It is the goal of this research to quantify the fate and transport of a suite of 2378-TCDD isomers in natural soils using batch and miscible-displacement experiments in order to understand the fate and transport of the toxic 2378-TCDD. Several nontoxic 2378-TCDD isomers exist that have similar chemical structure, and physical and chemical properties. Experiments with these isomers can help identify what happens to 2378-TCDD as it undergoes multiple fate and transport processes in soil, and can help to identify how various soil fractions influence these processes. Also, these experiments can provide information about the potential impacts of 2378-TCDD on soils and subsurface water resources. The isomers that were used were [4-¹⁴C]-radiolabeled 1278-TCDD, 1378-TCDD, and 1478-TCDD. They were used because they are nontoxic and can be used in experiments with little or no worry of toxic exposure, they can be considered prototypes for the fate and transport of 2378-TCDD, and since they are radiolabeled, they are easily identified even when they undergo metabolism. Inverse modeling was used to help describe and understand the fate and transport processes observed in the experimental results.

2. Materials and methods

The materials and methods that were used for the batch and miscible-displacement experiments were similar to an earlier study that identified the fate and transport of 17 β -estradiol (Casey et al., 2003). The soils that were used were from the surface A-horizon and were all collected in North Dakota, USA. The soil taxonomy and some physical properties are presented in Table 1.

2.1. Batch sorption experiments

Batch experiments were all run in triplicate. Oven dried (80 °C for 24 h), sieved (2 mm) soil, and a weak salt solution (0.01 M CaCl₂) were added to 10-mL vials in a ratio of 1.6 g of soil to 8 mL of 0.01 M CaCl₂.

Table 1

Soils and their major physical/chemical properties^a, which were used for the batch and miscible-displacement experiments

Soil series	Taxonomic description	Organic matter (%)	Specific surface (m ² g ⁻¹)	pH
Bearden-Silty clay loam ^b	Fine-silty, mixed, superactive, frigid aerice calciaquolls	7.50	175	7.90
Gardena-Clay loam ^b	Coarse-silty, mixed, superactive, frigid aerice calciaquolls	5.30	154	8.20
Glyndon-Sandy clay loam ^a	Coarse-silty, mixed, superactive, frigid aerice calciaquolls	3.30	123	7.60
LaDelle-Silt loam ^b	Fine-silty, mixed, superactive, frigid cumulic hapludolls	9.20	151	9.20
Renshaw-Loam ^b	Sandy-skeletal, mixed, frigid entic hapludolls	7.50	106	7.90
Sand ^c		0.00	—	—

^a Major physical and chemical properties of each soil type were measured at the Soil and Water Environmental Laboratory at North Dakota State University.

^b Obtained from Ag-Vise Company (Northwood, ND).

^c Obtained from J.T. Baker Chem. Company (Phillipsburg, NJ, Catalog No. 3382-5).

Several initial concentrations (0.006, 0.063, and 0.629 mg L⁻¹ for 1278-TCDD; 0.006, 0.063, and 0.629 mg L⁻¹ for 1378-TCDD; and 0.007, 0.073, 0.1, and 0.724 mg L⁻¹ for 1478-TCDD) of [4-¹⁴C]-radiolabeled TCDDs (ChemSyn Science Laboratories, Lenexa, KS) were used. These soil–water slurries were then agitated by rotating the vials from top to bottom (36° every 5 seconds). After 48, 96, and 168 h for 1278-TCDD and 1378-TCDD, and after 0.5, 1, 5, 24, 48, and 168 h for 1478-TCDD, the bottles were centrifuged at 1700 rpm (380×g for 20 min), and triplicate 100-μL aliquots were removed and assayed for radioactivity by liquid scintillation counting using a 1900 CA scintillation counter (Packard, Downers Grove, IL).

2.2. Miscible-displacement experiments

The oven dried and sieved soils (Table 1) were each evenly packed into individual glass columns (diameter=8.4 cm, length=15.2 cm) with stainless steel end-caps. Sandwiched between the soil and the end-caps were 40-mesh stainless steel screen and six layers of cheesecloth, which helped retain the soil. Table 2 provides the major physical properties of each column.

Each column was slowly wetted with a weak salt solution (0.01 M CaCl₂) from the bottom over a 24 h period. A weak salt solution was used so soil aggregates would not be dispersed. After saturation was achieved, water flow was established from the top down using the same 0.01 M CaCl₂ solution. Once steady-state pore water velocity (*v*) through the column (Table 2) was achieved (i.e., the *v* was constant), a pulse (Table 2) of higher CaCl₂ solution (0.05 M CaCl₂) was passed through the column and eluted with the 0.01 M CaCl₂ solution. The column effluent was fraction collected every 2 min, and the conductivity of each fraction 100 was measured using a conductivity meter (Oakton PC 300, Vernon Hills, IL). This 0.05 M CaCl₂ breakthrough

experiment provided information about the transport of a nonsorbing solute through the soil.

Following this chloride ion breakthrough curve experiment, a pulse of one of the [4-¹⁴C]-TCDDs (approximately 1.0 μCi, 5.0 μg) was applied to the surface of the column in 40 mL of 0.01 M CaCl₂ and eluted with at least 4.4 L of 0.01 M CaCl₂. The column effluent was fraction collected every 2 min, and each fraction was analyzed for ¹⁴C using the liquid scintillation. Thin-layer chromatography (TLC) [System 2000 Imaging Scanner (Bioscan, Inc., Washington, DC)] was also used to determine the presence of any TCDD metabolites in the column effluent, which could indicate whether any metabolism occurred.

Additionally, distributions of resident ¹⁴C in the column were determined. This was done by extruding the soil from each column in 1-cm increments, drying the soil, and assaying it for ¹⁴C by combustion analysis on a Packard Model 307 Oxidizer (Meriden, CT). Analysis for metabolites was also done on these extracts using TLC. A total of eighteen column experiments were done where there were three TCDD compounds and six soil materials.

2.3. Batch sorption model

A linear sorption isotherm was used to describe the batch experiment data, where the relationship between adsorbed concentration, *S* (mg g⁻¹), and the dissolved concentration, *C* (mg L⁻¹), is expressed as

$$S = K_d C \quad (1)$$

K_d (L g⁻¹) is a distribution coefficient.

Also a first-order rate constant, *β*, was determined for one of the TCDDs, 1478-TCDD using the following equation:

$$C(t) = C_0 e^{-\beta t} \quad (2)$$

Table 2
Soil column physical properties

Soil series	w^a (g)	θ^b (cm ³ cm ⁻³)	Pore volume (PV) (mL)	v^c (cm min ⁻¹)		Pulse input (relative PV)	
				Cl ⁻ BTC ^d	Dioxin BTC	Cl ⁻ BTC	Dioxin BTC
<i>1278-TCDD</i>							
Bearden-Silty clay loam	900	0.63	520	0.31	0.34	3.11	0.08
Gardena-Clay loam	740	0.71	590	0.29	0.31	2.69	0.07
Glyndon-Sandy clay loam	920	0.70	580	0.31	0.30	2.51	0.07
LaDelle-Silt loam	710	0.66	550	0.29	0.31	2.42	0.07
Renshaw-Loam	950	0.76	630	0.29	0.29	2.31	0.06
Sand	1420	0.40	330	0.21	0.51	3.88	0.12
<i>1378-TCDD</i>							
Bearden-Silty clay loam	851	0.69	574	0.33	0.31	3.15	0.07
Gardena-Clay loam	675	0.92	765	0.24	0.23	2.54	0.05
Glyndon-Sandy clay loam	847	0.56	466	0.40	0.42	3.49	0.09
LaDelle-Silt loam	654	0.72	599	0.29	0.31	2.41	0.07
Renshaw-Loam	937	0.60	499	0.37	0.39	3.20	0.08
Sand	1370	0.38	316	0.56	0.58	4.77	0.13
<i>1478-TCDD</i>							
Bearden-Silty clay loam	833	0.55	457	0.39	0.20	3.56	0.09
Gardena-Clay loam	771	0.78	648	0.28	0.22	2.35	0.06
Glyndon-Sandy clay loam	870	0.85	707	0.24	0.24	2.30	0.06
LaDelle-Silt loam	737	0.72	599	0.32	0.22	2.55	0.07
Renshaw-Loam	783	0.72	599	0.31	0.31	1.77	0.07
Sand							

^a Weight of dry soil (w).

^b Volumetric water content (θ).

^c Steady-state pore water velocity (v).

^d Breakthrough curve (BTC).

where C_0 is the initial concentration, and $C(t)$ is the solution concentration at time t (min). The time required for half the original mass of TCDD in aqueous phase to be adsorbed onto the solid phase ($t_{1/2}$) was also calculated for 1478-TCDD using the following equation:

$$t_{1/2} = \frac{\ln 2}{\beta}. \quad (3)$$

2.4. Miscible-displacement model

The computer software HYDRUS-1D (Šimůnek et al., 1998) was used to model the nonequilibrium transport of all the TCDD miscible displacement experiments. HYDRUS-1D uses a least-square optimization routine to fit the model to observed data by minimizing an objective function, which expresses the divergence between the observed and fitted data.

In order to describe the soil column transport data of the three TCDDs, a fully kinetic sorption transport model (Selim et al., 1977; van Genuchten and Wagenet, 1989) with linear sorption was used. The following

partial differential equation describes this transport model:

$$\frac{\partial C}{\partial t} + \frac{\rho_b}{\theta} \frac{\partial S}{\partial t} = v\lambda \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x}, \quad (4)$$

$$\frac{\partial S}{\partial t} = \alpha(K_d C - S) \quad (5)$$

where x is distance (cm); t is time (min); θ is volumetric water content (cm³ cm⁻³); v is average pore water velocity (cm min⁻¹); C is the reduced volume-averaged solution concentration (mg L⁻¹); λ is the dispersivity (cm); ρ_b is soil bulk density (g cm⁻³); S is the total sorbed concentration (mg g⁻¹); α is the first-order rate sorption coefficient; and K_d is defined in Eq. (1).

3. Results and discussion

3.1. Batch experiments

The results of the batch experiment are summarized in Table 3. For all the soils, at 48 h nearly all of the

Table 3
Linear sorption isotherm parameters and fitted results

Soil series	Linear sorption	
	K_d (L g ⁻¹)	r^2
<i>1278-TCDD</i> ^a		
Bearden-silty clay loam	Total sorption (TS)	
Gardena-clay loam	TS	
Glyndon-sandy clay loam	TS	
LaDelle-silt loam	TS	
Renshaw-loam	TS	
Sand	TS	
<i>1378-TCDD</i>		
Bearden-silty clay loam	1.77	0.98
Gardena-clay loam	1.31	1.00
Glyndon-sandy clay loam	1.79	0.99
LaDelle-silt loam	1.52	1.00
Renshaw-loam	1.21	1.00
Sand	1.00	0.99
<i>1478-TCDD</i>		
Bearden-silty clay loam	0.51	0.99
Gardena-clay loam	0.41	0.99
Glyndon-sandy clay loam	0.68	0.99
LaDelle-silt loam	0.46	1.00
Renshaw-loam	0.45	1.00
Sand	0.35	1.00

^a Values for 1278-TCDD were not determined because no aqueous concentrations were detected for the two lowest initial concentrations. There were however, aqueous concentrations detected for the highest initial concentrations. This indicated that sorption affinity was higher for 1278-TCDD than for the other two TCDDs even though the isotherm values could not be calculated.

TCDD was completely sorbed to the soil (≈ 98 –100%). Additional early-time sorption data for 1478-TCDD was obtained at 0.5, 1, 5, 24, 48, and 168 h to identify sorption reaction rates. Using Eqs. (2) and (3), the first-order rate constant, β , ranged from 0.04 min⁻¹ to 0.1 min⁻¹, and $t_{1/2}$ ranged from 7 min to 17 min for all of the soils. This indicated that the mass of 1478-TCDD would decrease to half the original mass in aqueous phase between 7 min and 17 min which is very rapid and can be considered nearly instantaneous. There was no aqueous concentration detected for 1278-TCDD when the initial concentrations were 0.059 and 0.006 mg L⁻¹; therefore, 1278-TCDD was more quickly adsorbed onto the solid soil than 1378-TCDD and 1478-TCDD.

Correlations of sorption to various soil fractions and properties (i.e., sand, silt, clay, OM, specific surface, and cation exchange capacity) were calculated. This was done by identifying the amount of TCDDs in the aqueous phase at 48, 96, and 168 h. Initially, for all the TCDDs there were significant negative correlations between OM and sorption, but the correlations increased

through time. The initial correlations at 48 h for 1278-TCDD ($r=-0.35$) and 1478-TCDD ($r=-0.18$) were weak, but increased at 168 h for both 1278-TCDD ($r=-0.77$) and 1478-TCDD ($r=-0.50$). The correlation for 1378-TCDD, however, was initially strong at 48 h ($r=-0.96$) and decreased by 168 h ($r=-0.25$). This rate-limited sorption may be evidenced by the relative change in aqueous 1378-TCDD concentrations through time for the soils with different OM contents (Fig. 2). At 48 h the aqueous concentrations of 1378-TCDD were higher for the soils with higher OM (i.e., LaDelle and Bearden in Fig. 2), but as time progressed (at 96 and 169 h) the aqueous 1378-TCDD concentrations decreased for these high OM soils. Fig. 2 also indicates that for the long term sorption data, between 96 h and 168 h, more 1378-TCDD was present in the aqueous phase for soils with lower OM than from soils with higher OM. The higher aqueous phase concentrations at longer times may indicate some desorption of the 1378-TCDD from the sorbed phase to the aqueous phase.

When kinetic sorption was considered with our data, the results compared well with the studies by Dougherty et al. (1991) and Overcash et al. (1991), who found that 2378-TCDD was tightly bound to soils with high OM. Their results also indicated that 2378-TCDD sorption is consistent with hydrophobic theory. In the current study, it took time for the TCDD isomers to fully sorb to the soils with high OM; however, after longer times (≥ 96 h) the TCDD became strongly sorbed for these soils. Walters and Guiseppi-Elie (1988) did research with 2378-TCDD using batch experiments and also found that it rapidly approached sorption equilibrium for soil with lower OM, but took significantly longer contact times for soil with higher OM. In the current and other studies it has been found that OM is a major factor in the

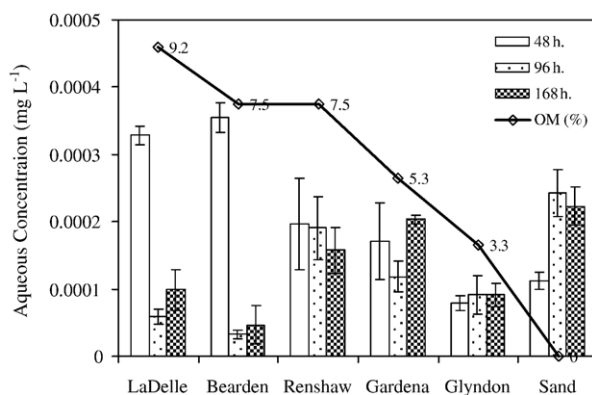


Fig. 2. The correlation between percent organic matter (OM%) and the amount of 1378-TCDD in the aqueous phase for each sample time. The values on the solid line indicate the %OM.

sorption rate and affinity of TCDDs to soil. In our study, a longer contact time was required to approach sorption equilibrium of TCDDs in the high OM soils compared to low OM soils, and TCDDs were more tightly bound to high OM soils than low OM soils after longer periods of time (>96 h).

A possible cause of this negative correlation of sorption to OM is rate-limited sorption caused by the OM. Pignatello and Xing (1996) reviewed many major published studies on the causes of excessively long sorption equilibrium rates and put forth two models to explain the slow sorption: (1) the organic matter diffusion model (OMD) and (2) the sorption-retarded pore diffusion model (SRPD). (1) The OMD considers soil organic matter (SOM) as synthetic organic polymers, which have glassy (condensed, rigid) or rubbery (expanded, flexible) structures with respect to the order and cohesive forces of the polymer chains. Each phase has a dissolution domain, but the glassy phase additionally contains holes in which the incoming contaminants undergo Langmuir-like sorption in voids internal to the polymer matrix. (2) The SRPD model postulates that the contaminant diffusion in pore water is retarded by local sorption on pore walls with little SOM. The rate of diffusion depends on the square of the particle radius, the tortuosity of pores, the constrictivity in the pores, and the K_d . Another factor that may contribute to the rate limited sorption is that complexing agents such as soluble organic carbon that may desorb from the solids and, in turn, compete with the adsorbate for the available sorption surface sites. Such effects increase when soil has a higher OM (EPA, 1999).

Thin layer chromatography could not be used to determine the presence of metabolites in the solution phase because of a lack of radioactivity left in the solution phase. The aqueous phase samples from these experiments were saved for possible analysis using more sensitive analytic instrumentation (e.g., mass-spectrophotometer). However, it was not likely that metabolism of the TCDD isomers occurred over the duration of the experiments because no metabolites of any TCDD were detected in the sorbed phase or effluent of the column experiments. Also other studies have shown TCDD were persistent in soil (Kapila et al., 1989; Vasquez et al., 2004).

3.2. Miscible-displacement experiments

The range of ^{14}C recovered (0.02–41%) in the column effluent from miscible-displacement experiments (Table 4) was very low, which indicated strong sorption for all the TCDD isomers. There was

essentially no 1478-TCDD present in any of the column effluents, which indicated stronger sorption compared to the other TCDDs tested. Soil combustion analyses revealed the vertical distribution of the TCDDs in the soil columns and indicated that most of the TCDDs applied were sorbed in the top 1–5 cm of each column (approximately 20–100% of the total mass applied). This result indicated that the TCDDs could be initially distributed vertically through the topsoil, and then little significant movement would occur through time.

All the effluent breakthrough curves of each TCDD and soil were asymmetric (Fig. 3), where the peak concentrations were shifted to the left and there were long effluent tails. This breakthrough curve shape indicates that solute arrives in the effluent early and bleeds off the column as a result of either a physical nonequilibrium or a chemical nonequilibrium processes. Physical nonequilibrium would be caused by transport through secondary soil physical structures, such as macropores, or by fingering. Chemical nonequilibrium transport would be caused by rate-limited sorption, as suggested by our batch data. Das et al. (2004) showed similar asymmetric breakthrough curves (i.e., peak shifted to the left and long tails) that were caused by chemical nonequilibrium transport. The TCDD breakthrough peaks (at less than one-pore volume) were all earlier than the chloride ion breakthrough peaks. All the chloride ion breakthrough curves were symmetrical, which indicated that transport was a physical-equilibrium, convective dispersive process. The equilibrium convective-dispersive model provided an excellent description of the chloride transport (coefficient of determination (r^2) values ranged from 0.95 to 0.99) when $k_d \neq 0$ (i.e., no sorption of chloride). The model results and shape of the chloride breakthrough curves indicated that physical nonequilibrium transport was not a contributing factor for the observed transport of the TCDDs. Rather, the observed nonequilibrium of the TCDD breakthrough curves was likely caused by chemical factors (e.g., kinetic sorption). Another explanation for the early arrival of strongly sorbed TCDDs was the possibility of colloidal-facilitated transport, which is discussed in a later section.

The TLC results indicated that no TCDD metabolites were present in the effluent of any of the soil columns. Also, the TLC analyses from the extracts of the soil from within the columns indicated that there were no metabolites present in the sorbed phase. This result indicated that although the TCDDs were strongly sorbed, they persisted with little or no transformation, which indicated that degradation of TCDDs on soil did not readily occur. This result might be due to the

Table 4

Miscible-displacement parameter estimates for the fate and transport of 1278-TCDD, 1378-TCDD, and 1478-TCDD with 95% confidence interval (in parentheses)

Soil series	λ (cm)	K_d (L g ⁻¹)	α (min ⁻¹)	r^2	% ¹⁴ C Recovery	
					Effluent	Total
<i>1278-TCDD</i>						
Bearden-Silty clay loam	8.00	1.14	1.00E-4 (<1.00E-5)	0.80	15.07	76.33
Gardena-Clay loam	11.06	0.86	2.00E-4 (<1.00E-5)	0.98	15.86	57.53
Glyndon-Sandy clay loam	0.21 (±0.0009)	1.24	7.00E-5 (<1.00E-5)	0.87	41.20	NA
LaDelle-Silt loam	6.90	0.99	1.00E-4 (<1.00E-5)	0.80	18.08	81.60
Renshaw-Loam	12.90	0.83	6.00E-4 (±2.00E-5)	0.96	0.63	118.96
Sand	NA ^a	NA	NA	NA	0.35	54.35
<i>1378-TCDD</i>						
Bearden-Silty clay loam	5.64	1.77	2.00E-4 (<1.00E-5)	0.93	1.07	102.12
Gardena-Clay loam	14.56	1.31	1.00E-4 (±1.00E-5)	0.80	26.90	76.80
Glyndon-Sandy clay loam	NA	NA	NA	NA	0.02	NA
LaDelle-Silt loam	6.71	1.52	7.00E-5 (<1.00E-5)	0.98	24.90	64.50
Renshaw-Loam	6.21	1.21	2.00E-4 (±1.00E-5)	0.80	1.38	70.53
Sand	NA	NA	NA	NA	0.66	77.09
<i>1478-TCDD</i>						
Bearden-Silty clay loam	NA	NA	NA	NA	0.04	95.20
Gardena-Clay loam	NA	NA	NA	NA	0.64	83.78
Glyndon-Sandy clay loam	NA	NA	NA	NA	0.16	72.56
LaDelle-Silt loam	3.11	0.46	5.00E-4 (±2.00E-5)	0.76	0.99	76.06
Renshaw-Loam	NA	NA	NA	NA	0.61	90.65
Sand	NA	NA	NA	NA	NA	NA

^a The NA indicates that no model fits were obtained because little or no solute was present in the column effluent.

difficulty in cleaving a carbon-chlorine bond from an aromatic ring (Timbrell, 2003). The persistence of TCDD in soil is also supported by Kapila et al. (1989) who conducted soil column experiments to study the movement of TCDD under field and laboratory conditions. Their results indicated that TCDD was very persistent in the soil and no significant degradation of 2378-TCDD was observed. Also, Vasquez et al. (2004) used surface soil concentration of TCDD observed in 1984 to predict the concentration of TCDD in 2054 using the model CalTOX. They found that more than 94% of TCDD observed in the surface soils in 1984 will remain in the soil after a 70-year period.

3.2.1. Miscible-displacement model results.

The fully kinetic sorption transport model (Eqs. (4) and (5)) was fitted to the TCDD effluent data. For the modeling of the TCDD breakthroughs, the initial values of dispersivity, λ , were set equal to the λ values obtained from the chloride breakthrough. Also, the initial column distribution coefficient, K_d , values were set equal to the K_d values obtained from the batch experiments. For the TCDD, the only parameter that

was estimated was α . The exception was the Glyndon soil where it was necessary to fit λ to obtain a good fit. These model results indicated a consistency between batch, and chloride and TCDD column experiments. The optimized transport parameter estimates are presented in Table 4.

For all the soil column experiments, sorption was dominated by a kinetic process with little or no observable instantaneous sorption. The sand columns also had little TCDD present in the column effluent. Schwarzenbach and Westall (1981) have shown that significant sorption of nonpolar organic compounds can occur in materials with little or no organic fractions, where micropores in the silica are the major cause of this sorption.

The kinetic rate-limited sorption results that were observed for the column studies were supported by the batch experiments. For the batch studies, it was found that TCDDs were strongly sorbed; yet, it took time to achieve full sorption especially in soils with higher OM. The first-order sorption rate coefficients (α) determined from the column experiments were much smaller than the batch experiment β values. It is likely that this rate-limited sorption was caused by a diffusive transport

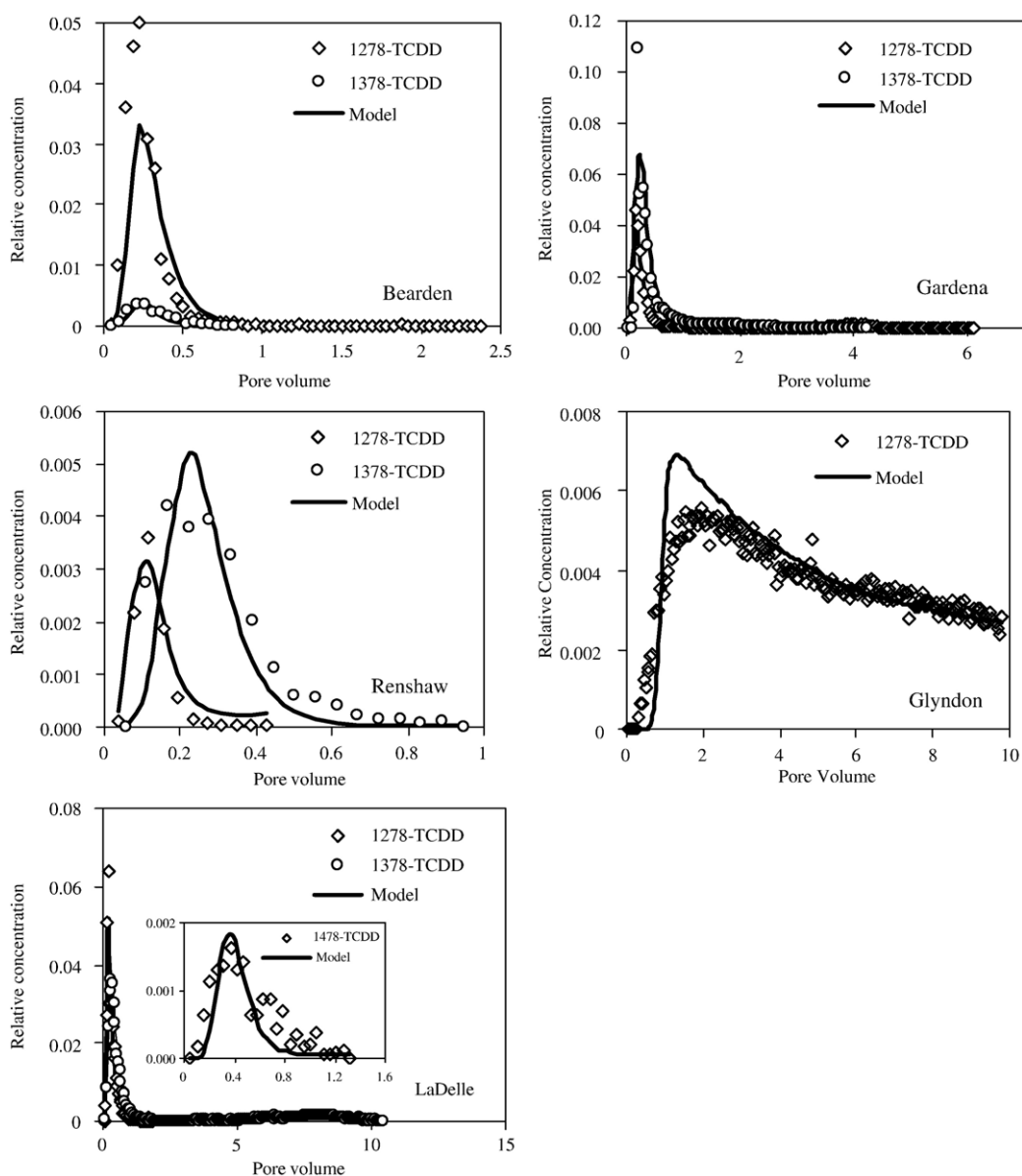


Fig. 3. TCDDs column breakthrough curves and corresponding model fits for each soil.

from the bulk solution and/or through OM (Pignatello and Xing, 1996) to the sorption site. If this is the case, then differences between the batch and column kinetics are expected. The contact times with the soil for the column experiments only ranged between 63 and 72 min (compared to 48–168 h for the batch experiment), which probably was not enough time to sorb all the TCDD. Moreover, the advective flow in the soil pores could also reduce the diffusive exchange of solute to the sorbed phases, thus causing a smaller α value compared to the β values from the batch experiments.

The asymmetric breakthrough curves with long elution tails could only be modeled if the α term, albeit small, was considered.

3.2.2. Colloidal transport

Although colloidal transport was less likely to contribute significantly to the fate and transport of the TCDD isomers, it should be considered as a possible explanation. Colloids are high surface area particles with diameters less than 10 μm , and are created within the soil by detachment from the static soil matrix

(McGechan and Lewis, 2002). The detachment mechanisms of colloids are not fully understood and occur more readily under saturated conditions. For our experiments more than ten pore volumes of water was passed through the columns before the actual TCDD solution was applied. At the time the TCDD was applied, it would seem that most or all the colloids would have been detached from the soil. Nonetheless, this colloidal transport theory may explain some of the data we observed.

Colloidal-facilitated transport might be partly responsible for the early eluting breakthrough peaks of the TCDD (Fig. 3). A number of authors using soil columns or lysimeter experiments have measured some detachment of such particles when water passes through the soil (Kaplan et al., 1993; Jacobsen et al., 1997). Colloids suspended in water can act as a mobile or flowing solid phase, which can adsorb contaminants in a fashion similar to the immobile or stagnant solid phase, but can migrate at rates similar to, or even greater than, the mobile aqueous phase (McGechan and Lewis, 2002). Grolimund et al. (1996) reported that colloid-facilitated transport provided the dominant transport pathway for rapid transport of a strongly sorbed contaminant using a laboratory column study. Their results indicate that a transport model, which neglected the colloid mobilization, dramatically underestimated the total effluent concentration of contaminant and its travel velocity by several orders of magnitude. Field observations have shown that polychlorinated dibenzo-*p*-dioxins moved faster through soils than would be expected based on their solubility (Walters et al., 1989b), which may be a result of colloidal transport or some physical or chemical nonequilibrium process such as the rate-limited sorption discussed earlier.

The results of the combustion analyses showed that there was a strong correlation between specific surface and the redistribution of TCDDs in soil columns (Fig. 4). The correlations in Fig. 4 possibly point toward a colloidal transport mechanism for the soils with high specific surface, because soils with higher specific surface are known to have more colloidal particles. Fig. 4 shows the correlations between the specific surface of the soil and the amount TCDD sorbed to the top 1–5 cm of the column and also the bottom 11–15 cm of the column. For each soil column the specific surface had a strong negative correlation to the amount of TCDD sorbed to top 1–5 cm of soil. Also, there were corresponding positive correlations between specific surface and total TCDD sorbed at the bottom 11–15 cm of these same soil columns. These correlations suggest that soil columns with higher specific surface (i.e. soils

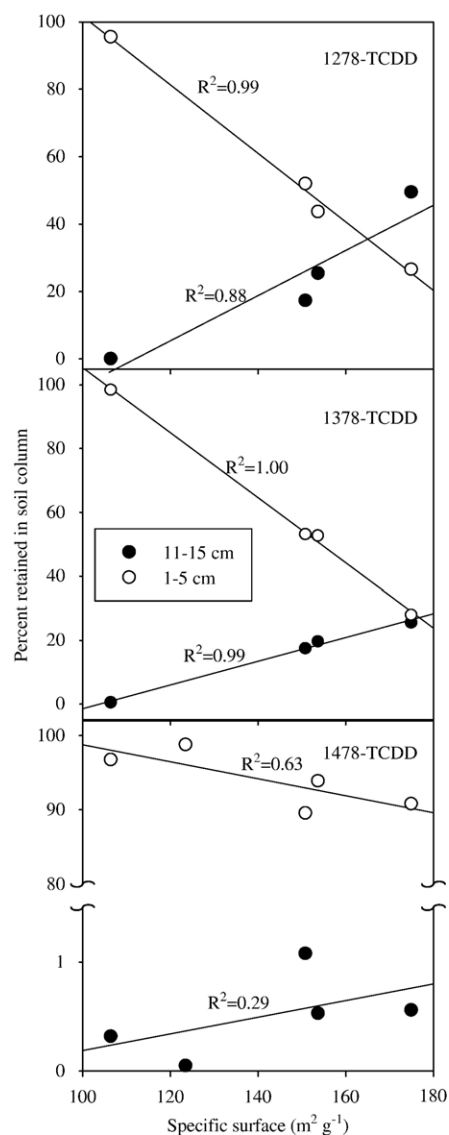


Fig. 4. The correlation between specific surface and percent TCDD sorbed to the top 1–5 cm and 11–15 cm soil in columns.

with more colloids) will have more TCDD transported out of the top 5 cm of soils and deposited into the bottom 11–15 cm depths. Conversely, for the soils with the lower specific surface values (i.e. less colloids), the TCDD will tend to stay in the upper 1–5 cm of soil and not migrate to the bottom 11–15 cm of the soil column. This result indicates that it was quite possible that some of the TCDDs were redistributed through the columns by colloidal transport, as demonstrated by Ryan and Elimelech (1996) who found that colloids act as pollutant carriers that can increase the amount of TCDDs in flowing water. A complete understanding of contaminant–colloid interactions at the molecular

level will be required to accurately assess the environmental fate of dioxins (McGechan and Lewis, 2002). Future studies need to be performed to determine the occurrence and mobility of subsurface colloids and their potential effect on the transport of non-polar contaminants, such as dioxins.

4. Conclusion

The batch experiments and miscible-displacement experiments indicated that the 1278-TCDD, 1378-TCDD, and 1478-TCDD were all strongly sorbed to the soil and that OM was significant in the strength and rate of sorption. In general, sorption equilibrium was achieved earlier for the lower OM soils than the higher OM soils. A fully kinetic sorption miscible-displacement model with no degradation was successfully used to describe the fate and transport of the TCDD isomers. In spite of the TCDDs low water solubility and strong sorption affinity, small amounts were still eluted from the soil columns and significant amounts were redistributed through the columns. The soil extraction and combustion analyses indicated that there was strong correlation between specific surface and the vertical distribution of TCDDs in soil columns. This correlation may indicate that TCDD can be redistributed in soil by colloid-facilitated transport.

These findings are important in understanding the fate and transport of the toxic TCDD sibling, 2378-TCDD. Previous studies contend that under most environmental conditions, the impact of 2378-TCDD-contaminated soil on underlying groundwater is not expected to be important (EPA, 1986; Vasquez et al., 2004). In our study we did find that sorption of these TCDD isomers was very rapid, yet they can be redistributed in soils with higher specific surface, and may be transported to a greater extent than previous predicted. Our results also indicated that TCDDs may migrate deeper in soils with different OM and soil-water velocity. This potential for migration can be further exacerbated due to the historical deposition and accumulation of TCDDs into the soils. Although our results were generated under boundary conditions that are extreme under natural conditions (they are likely to present exaggerated results), they underline the importance for an improved understanding of the dynamics TCDD dioxin fate and transport in soil-water systems. An improved understanding of physical and chemical nonequilibrium transport as well as facilitate transport is needed to help to predict the migration of 2378-TCDD and development of strategies for its remediation.

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